

WHAT IS CLAIMED IS:

1 1. A liquid stereolithography resin comprising a first urethane acrylate oligomer,
2 a first acrylate monomer, and a polymerization modifier.

1 2. The liquid stereolithography resin of claim 1, further comprising a
2 photoinitiator.

1 3. The liquid stereolithography resin of claim 2, wherein the photoinitiator
2 includes a phosphine oxide, an alpha-hydroxyketone, and a benzophenone derivative.

1 4. The liquid stereolithography resin of claim 2, wherein the photoinitiator
2 includes a component selected from the group consisting of a benzophenone, a benzil
3 dimethyl ketal, a 1-hydroxy-cyclohexylphenylketone, an isopropyl thioxanthone, an ethyl 4-
4 (dimethylamino)benzoate, SARCURE SR1135, a benzoin normal butyl ether, SARCURE
5 SR1130E, tripropyleneglycol diacrylate, an oligo(2-hydroxy-2-methyl-1-(4-(1-
6 methylvinyl)phenyl)propanone), a 2-hydroxy-2-methyl-1-phenyl-1-propanone, a poly(2-
7 hydroxy-2-methyl-1-phenyl-1-propanone), a trimethylolpropane triacrylate, a SARCURE
8 SR1137, a SARCURE SR1130, a phosphine oxide, a 4-methylbenzophenone, a
9 trimethylbenzophenone, a methylbenzophenone, a Darocur 4265, and an Irgacure.

1 5. The liquid stereolithography resin of claim 2, wherein the photoinitiator
2 includes a component selected from the group consisting of a Darocur 4265, a phosphine
3 oxide, a 2-hydroxy-2-methyl-1-phenyl-1-propanone, and mixtures thereof.

1 6. The liquid stereolithography resin of claim 2, wherein the photoinitiator
2 activates polymerization of an acrylate in a wavelength range of 240 nm to 250 nm, 360 nm
3 to 380 nm, or 390 nm to 410 nm.

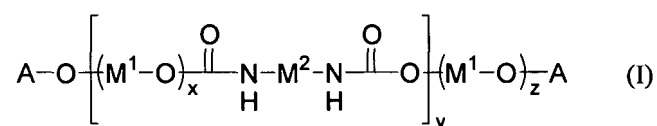
1 7. The liquid stereolithography resin of claim 1, wherein the first urethane
2 acrylate oligomer includes a polyester urethane diacrylate.

1 8. The liquid stereolithography resin of claim 7, wherein the polyester urethane
2 diacrylate is an aliphatic polyester urethane diacrylate.

1 9. The liquid stereolithography resin of claim 1, wherein the first acrylate
2 monomer includes a monovalent acrylate.

1 10. The liquid stereolithography resin of claim 1, wherein the first acrylate
2 monomer includes a polyvalent acrylate.

1 11. The liquid stereolithography resin of claim 1, wherein the first urethane
2 acrylate oligomer has formula (I):

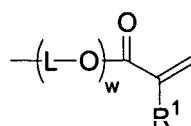


3
4 wherein

5 each M^1 is, independently, an alkylene, an acylalkylene, an oxyalkylene, an arylene,
6 an acylarylene, or an oxyarylene, M^1 being optionally substituted with alkyl, cycloalkyl,
7 alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino,
8 silicone, aryl, or aralkyl,

9 each M^2 is, independently, an alkylene or an arylene, M^2 being optionally substituted
10 with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl,
11 halo, haloalkyl, amino, silicone, aryl, or aralkyl,

12 each A, independently, has the formula:



13
14 wherein R^1 is hydrogen or lower alkyl, each L is, independently, C_1 - C_4 alkyl, and w is
15 an integer ranging from 0 to 20, and

16 x is a positive integer less than 40, y is a positive integer less than 100, z is a positive
17 integer less than 40, and w, x, y, and z together are selected such that the molecular weight of
18 the first urethane acrylate oligomer is less than 20,000.

12. The liquid stereolithography resin of claim 11, wherein M¹ is a straight, branched, or cyclic alkylene.

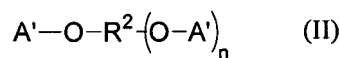
13. The liquid stereolithography resin of claim 11, wherein M¹ is an acylalkylene or acylarylene.

14. The liquid stereolithography resin of claim 13, wherein M² is a straight, branched, or cyclic alkylene.

15. The liquid stereolithography resin of claim 11, wherein M^2 is a straight, branched, or cyclic alkylene.

16. The liquid stereolithography resin of claim 11, wherein L is branched or unbranched C₁-C₄ alkyl.

17. The liquid stereolithography resin of claim 11, wherein the first acrylate monomer has formula (II):

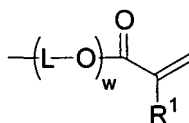


wherein

R² is a monovalent or polyvalent moiety selected from the group consisting of a C₁-C₁₂ aliphatic group, an aromatic group, and a poly(C₁-C₄ branched or unbranched alkyl ether), R² being optionally substituted with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, aryl, or aralkyl,

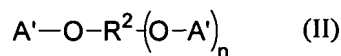
n is an integer ranging from 0 to 5, and

each A' has the formula:



wherein R¹ is hydrogen or lower alkyl, each L independently is C₁-C₄ alkyl, and w is an integer ranging from 0 to 20.

18. The liquid stereolithography resin of claim 1, wherein the first acrylate monomer has formula (II):

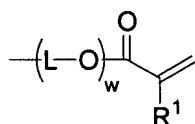


wherein

R² is a monovalent or polyvalent moiety selected from the group consisting of a C₁-C₁₂ aliphatic group, an aromatic group, and a poly(C₁-C₄ branched or unbranched alkyl ether), R² being optionally substituted with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, aryl, or aralkyl,

n is an integer ranging from 0 to 5, and

each A' has the formula:

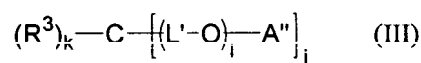


wherein R¹ is hydrogen or lower alkyl, each L independently is C₁-C₄ alkyl, and w is an integer ranging from 0 to 20.

19. The liquid stereolithography resin of claim 18, wherein L is branched or unbranched C₁-C₄ alkyl.

20. The liquid stereolithography resin of claim 1, wherein the polymerization modifier includes a second acrylate monomer.

21. The liquid stereolithography resin of claim 20, wherein the second acrylate monomer has formula (III):



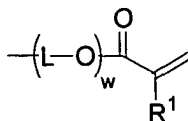
wherein

j is 1, 2, 3 or 4,

k is equal to 4-j,

R³ is hydrogen or C₁-C₄ branched or unbranched alkyl, each L' independently is C₁-C₄ branched or unbranched alkyl, each i independently is 0, 1, 2 or 3, and

each A'' independently has the formula:



wherein R^1 is hydrogen or lower alkyl, each L independently is $\text{C}_1\text{-C}_4$ branched or unbranched alkyl, and w is an integer ranging from 0 to 20.

22. The liquid stereolithography resin of claim 1, wherein the polymerization modifier includes a second urethane acrylate oligomer.

23. The liquid stereolithography resin of claim 1, wherein the polymerization modifier is selected from the group consisting of a trimethylolpropane triacrylate, a bisphenol A dimethacrylate, a tripropyleneglycol diacrylate, a pentaerythritol tetraacrylate, a 2-(2-ethoxyethoxy)ethylacrylate, a tris(2-hydroxyethyl)isocyanurate triacrylate, an isobornyl acrylate, and mixtures thereof.

24. The liquid stereolithography resin of claim 1, wherein the polymerization modifier includes isobornyl acrylate.

25. The liquid stereolithography resin of claim 1, further comprising a stabilizer.

26. The liquid stereolithography resin of claim 25, wherein the stabilizer is selected from the group consisting of Tinuvin 292 (bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate and 1-methyl-10-(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate), Tinuvin 765 (bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate), MEQH (4-methoxyphenol), LA-32, LA-82 and Chimassorb 81 (2-hydroxy-4-octyloxybenzophenone).

27. The liquid stereolithography resin of claim 1, wherein the first urethane acrylate oligomer is Sartomer CN964, the first acrylate monomer is Sartomer SR454, and the polymerization modifier is selected from the group consisting of Sartomer SR506, Sartomer SR494, Sartomer CN965, Sartomer SR368, and mixtures thereof.

28. The liquid stereolithography resin of claim 27, wherein the resin includes 5-35 weight % Sartomer CN964 and 0.5-25 weight % Sartomer SR454.

1 29. The liquid stereolithography resin of claim 28, wherein the resin includes 0.5-
2 20 weight % Sartomer SR506.

1 30. The liquid stereolithography resin of claim 28, wherein the resin includes 15-
2 45 weight % Sartomer SR494.

1 31. The liquid stereolithography resin of claim 28, wherein the resin includes 0.5-
2 25 weight % Sartomer CN965.

1 32. The liquid stereolithography resin of claim 28, wherein the resin includes 5-35
2 weight % Sartomer SR368.

1 33. The liquid stereolithography resin of claim 1, wherein the first urethane
2 acrylate oligomer is Sartomer CN963, the first acrylate monomer is Sartomer SR306, and the
3 polymerization modifier is selected from the group of Sartomer CN970H75, Sartomer
4 CD540, Sartomer SR506, and mixtures thereof.

1 34. The liquid stereolithography resin of claim 33, wherein the resin includes 40-
2 70 weight % Sartomer CN963, and 5-35 weight % Sartomer SR306.

1 35. The liquid stereolithography resin of claim 34, wherein the resin includes 0.5-
2 15 weight % Sartomer CN970H75.

1 36. The liquid stereolithography resin of claim 34, wherein the resin includes 0.5-
2 15 weight % Sartomer CD540.

1 37. The liquid stereolithography resin of claim 34, wherein the resin includes 5-35
2 weight % Sartomer SR506.

1 38. The liquid stereolithography resin of claim 1, wherein the first urethane
2 acrylate oligomer is Sartomer CN966, the first acrylate monomer is Sartomer SR506, and the
3 polymerization modifier is selected from the group consisting of Sartomer SR506, Sartomer
4 CD540, and mixtures thereof.

1 39. The liquid stereolithography resin of claim 38, wherein the resin includes 10-
2 40 weight % Sartomer CN966 and 0.5-25 weight % Sartomer SR506.

1 40. The liquid stereolithography resin of claim 38, wherein the resin includes 6-35
2 weight % Sartomer SR506.

1 41. The liquid stereolithography resin of claim 38, wherein the resin includes 25-
2 55 weight % Sartomer CD540.

1 42. The liquid stereolithography resin of claim 1, wherein the first urethane
2 acrylate oligomer is Sartomer CN990, the first acrylate monomer is Sartomer SR506, and the
3 polymerization modifier is selected from the group consisting of Sartomer CN131, BYK
4 Chemie BYK UV 3500, and mixtures thereof.

1 43. The liquid stereolithography resin of claim 42, wherein the resin includes 50-
2 80 weight % Sartomer CN990 and 0.5-20 weight % Sartomer SR506.

1 44. The liquid stereolithography resin of claim 43, wherein the resin includes 5-35
2 weight % Sartomer CN131.

1 45. The liquid stereolithography resin of claim 43, wherein the resin includes 0.5-
2 15 weight % BYK Chemie BYK UV 3500.

1 46. The liquid stereolithography resin of claim 1, wherein the first urethane
2 acrylate oligomer is Sartomer CN973, the first acrylate monomer is Sartomer SR506, and the
3 polymerization modifier is Sartomer SR506.

1 47. The liquid stereolithography resin of claim 46, wherein the resin includes 45-
2 75 weight % Sartomer CN973 and 10-70 weight % Sartomer SR506.

1 48. The liquid stereolithography resin of claim 1, wherein the first urethane
2 acrylate oligomer is Sartomer CN963, the first acrylate monomer is Sartomer SR306, and the

polymerization modifier is selected from the group consisting of Sartomer CN2400, Sartomer SR506, and mixtures thereof.

49. The liquid stereolithography resin of claim 48, wherein the resin includes 20-50 weight % Sartomer CN963 and 0.5-25 weight % Sartomer SR306.

50. The liquid stereolithography resin of claim 49, wherein the resin includes 10-40 weight % Sartomer CN2400.

51. The liquid stereolithography resin of claim 49, wherein the resin includes 10-40 weight % Sartomer SR506.

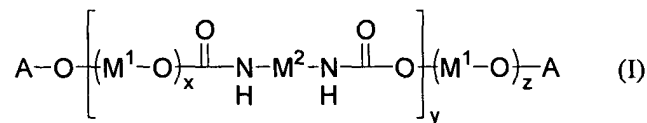
52. The liquid stereolithography resin of claim 1, wherein the first urethane acrylate oligomer is Sartomer CN966, the first acrylate monomer is Sartomer SR506, and the polymerization modifier is selected from the group consisting of Sartomer CN131 and Sartomer SR506.

53. The liquid stereolithography resin of claim 52, wherein the resin includes 35-60 weight % Sartomer CN966 and 10-25 weight % Sartomer SR506.

54. The liquid stereolithography resin of claim 52, wherein the resin includes 10-45 weight % Sartomer SR506.

55. The liquid stereolithography resin of claim 52, wherein the resin includes 5-35 weight % Sartomer CN131.

56. A liquid stereolithography resin comprising:
a first urethane acrylate oligomer having formula (I):

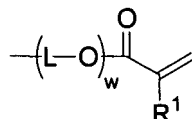


wherein

each M¹ is, independently, an alkylene, an acylalkylene, an oxyalkylene, an arylene, an acylarylene, or an oxyarylene, M¹ being optionally substituted with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, silicone, aryl, or aralkyl,

each M² is, independently, an alkylene or an arylene, M² being optionally substituted with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, silicone, aryl, or aralkyl,

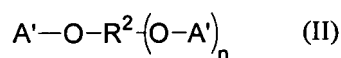
each A, independently, has the formula:



wherein R¹ is hydrogen or lower alkyl, each L is, independently, C₁-C₄ alkyl, and w is an integer ranging from 0 to 20, and

x is a positive integer less than 40, y is a positive integer less than 100, z is a positive integer less than 40, and w, x, y, and z together are selected such that the molecular weight of the first urethane acrylate oligomer is less than 20,000;

a first acrylate monomer having formula (II):

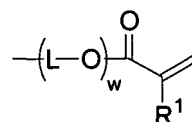


wherein

R² is a monovalent or polyvalent moiety selected from the group consisting of a C₁-C₁₂ aliphatic group, an aromatic group, and a poly(C₁-C₄ branched or unbranched alkyl ether), R² being optionally substituted with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, aryl, or aralkyl,

n is an integer ranging from 0 to 5, and

each A' has the formula:



wherein R¹ is hydrogen or lower alkyl, each L independently is C₁-C₄ alkyl, and w is an integer ranging from 0 to 20; and

32 a polymerization modifier including a second urethane acrylate oligomer, a second acrylate
33 monomer, or a combination thereof.

1 57. The liquid stereolithography resin of claim 56, further comprising a
2 photoinitiator and a stabilizer.

1 58. A method of forming a three-dimensional object comprising:
2 choosing a precursor based on a performance characteristic of a finished product,
3 wherein the performance characteristic is selected from the group consisting of hardness,
4 flexibility, dimensional stability, clarity, toughness, elasticity, heat resistance, weather
5 resistance, and combinations thereof;
6 mixing the precursor with a stock solution including a urethane acrylate oligomer and
7 an acrylate monomer to form a stereolithography resin; and
8 selectively exposing the resin to light to form a solidified layer.

1 59. The method of claim 58, wherein the stock solution includes a photoinitiator
2 and a stabilizer.

1 60. The method of claim 58, wherein the desired characteristic of the finished
2 product is dimensional stability and the precursor is isobornyl acrylate.

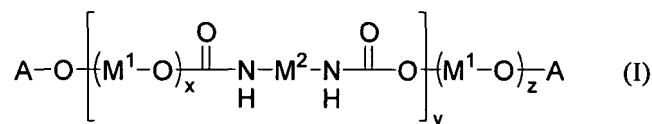
1 61. A method of forming a three-dimensional object comprising:
2 selectively exposing to actinic radiation a first portion of a resin including a first
3 urethane acrylate oligomer, a first acrylate monomer, and a polymerization modifier to form a
4 first solidified layer; and
5 selectively exposing to actinic radiation a second portion of the resin to form a second
6 solidified layer adjacent to the first solidified layer.

1 62. The method of claim 61, wherein the resin further includes a photoinitiator
2 and a stabilizer.

63. The method of claim 62, wherein the photoinitiator activates polymerization of an acrylate in a wavelength range of 240 nm to 250 nm, 360 nm to 380 nm, or 390 nm to 410 nm.

64. The method of claim 61, wherein the resin includes isobornyl acrylate.

65. The method of claim 61, wherein the first urethane acrylate oligomer has formula (I):

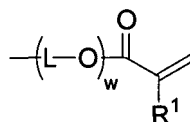


wherein

each M^1 is, independently, an alkylene, an acylalkylene, an oxyalkylene, an arylene, an acylarylene, or an oxyarylene, M^1 being optionally substituted with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, silicone, aryl, or aralkyl,

each M^2 is, independently, an alkylene or an arylene, M^2 being optionally substituted with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, silicone, aryl, or aralkyl,

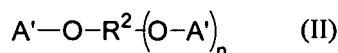
each A, independently, has the formula:



wherein R^1 is hydrogen or lower alkyl, each L is, independently, C_1 - C_4 alkyl, and w is an integer ranging from 0 to 20, and

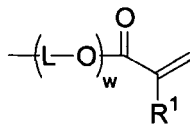
x is a positive integer less than 40, y is a positive integer less than 100, z is a positive integer less than 40, and w, x, y, and z together are selected such that the molecular weight of the first urethane acrylate oligomer is less than 20,000.

66. The method of claim 61, wherein the first acrylate monomer has formula (II):



wherein

4 R^2 is a monovalent or polyvalent moiety selected from the group consisting of a C_1 -
 5 C_{12} aliphatic group, an aromatic group, and a poly(C_1 - C_4 branched or unbranched alkyl
 6 ether), R^2 being optionally substituted with alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl,
 7 acyl, alkoxy, hydroxyl, hydroxylalkyl, halo, haloalkyl, amino, aryl, or aralkyl,
 8 n is an integer ranging from 0 to 5, and
 9 each A' has the formula:



10 wherein R^1 is hydrogen or lower alkyl, each L independently is C_1 - C_4 alkyl, and w is
 11 an integer ranging from 0 to 20.
 12

1 67. The method of claim 61, wherein the polymerization modifier includes a
 2 second urethane acrylate oligomer, a second acrylate monomer, or a combination thereof.